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**Performance enhancement of ultrafiltration membrane via simple deposition of  
polymer-based modifiers**

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## **Abstract**

Ultrafiltration (UF) membrane is extensively utilized in water treatment for the removal of colloidal particles, dissolved organic matters and microorganisms. These colloidal particles and organic matters are prone to being adsorbed on membrane surface known as membrane fouling, which increases operational costs and lowers down membrane efficiency. In this work, a group of synthesized hydrophilic random copolymers and homopolymer were utilized to enhance PES UF membrane performance by a simple deposition of a thin layer. Despite the increased intrinsic resistance as a result of the thin modification layer, higher pure water permeability and recovery rate were observed for the modified Polyethersulfone (PES) membrane during Bovine Serum Albumin (BSA) fouling test in comparison to the virgin membrane. Moreover, the stability of the adsorbed polymer layers was evaluated by a cyclic fouling test and chemical cleaning endurance assessment. The membrane surface morphology and topography were characterized by field emission scanning electron microscopy (FESEM) and atom force microscope (AFM). The chemical composition before and after cyclic fouling test and chemical cleaning were studied with attenuated total reflectance fourier transform infrared (ATR-FTIR) spectroscopy. The results show that the random copolymer modified membrane exhibited average 26% rises in water permeability compared with the virgin PES UF membrane when 0.5 wt % BSA solution was used as feed. The stable permeability and flux recovery rate during the cyclic study with chemical cleaning suggest good affinity of the newly synthesized random copolymer with the PES membrane and water. This strategy successfully enhanced the UF membrane anti-fouling performance.

**Keywords:** Ultrafiltration; copolymer; anti-fouling; adsorption.

**Research Highlights:**

- Synthesized polymers were robustly deposited on PES UF membrane surface.
- PES UF membrane antifouling performance was enhanced by the polymer deposition.
- The polymer increased intrinsic membrane resistance but reduced total resistance during fouling.
- The stability of the polymer layer during BSA fouling test and chemical cleaning were investigated.

## 1. Introduction

Membrane technologies play a vital role in the water treatment industry due to its high efficiency, small footprint, and low energy requirement for operation [1-3]. Ultrafiltration (UF) membranes allow the removal of colloidal particles, microorganisms and a considerable amount of dissolved organic matters especially those with the sizes in the micrometer range to purify water [4-6]. These membranes have been extensively utilized as an alternative technology to conventional water purification methods [7, 8]. However, UF membranes frequently hindered by membrane fouling, resulting from the undesirable deposition of organic matters on to the membrane surface and pores clogging, which in turn reduces the membrane efficiency, shortens membrane lifespan and increases operation cost [7, 9, 10]. Thus, the development of membranes with anti-fouling properties, easy cleaning, and high water productivity has become a matter of high priority in membrane technology.

It is well recognized that a membrane with hydrophobic, rough, highly positively charged surface exhibits high adsorption tendency to protein [11]. Therefore, modification of membrane surfaces to induce hydrophilic, smooth and negatively charged characteristics has been a significant focus for development of fouling-resistant membranes. So far, two major types of methodologies have been exploited to increase the hydrophilicity of UF membranes: (1) Antifouling materials are grafted onto membrane surfaces via a variety techniques including chemical posttreatment [12], UV irradiation [13] and plasma treatment; (2) Blending polymer materials with a more hydrophilic inorganic nanomaterials, polymers and amphiphilic copolymers [14-17] is another strategy to improve membrane hydrophilicity. Although the membrane's hydrophilicity can be enhanced for antifouling modification, these procedures usually are aggressive, tedious or incapable of large-scale production[18].

UF membrane fouling usually appears in a combination of mechanisms such as adsorption, pore blocking, and cake or gel formation [4, 19-21]. Adsorption of proteins and humic acids is a common problem encountered and often irreversible [10]. It is challenging to recover the membrane's water flux causing by internal fouling where the foulants are trapped inside porous

sublayers [22]. A more effective way to prevent or reduce fouling is to avoid the foulant from trapping into the membrane sublayer. The membrane separation process is a surface phenomenon where the skin/selective layer plays a pivotal role in retaining foulants. Thus, it is a natural option to alter the surface chemistry or topography of membranes for fouling control [23]. Among various approaches, a thin hydrophilic layer generated on membrane surface via deposition is a practical solution attributing to its simple procedure, low cost, easy to scale-up and its presence on the surface. This inert deposition layer could act as a prefilter to screen out those matters with a high propensity to cause membrane fouling [9, 10]. However, in most situations, the deposited material may leach out or be washed off after long time filtration or frequent chemical cleaning. The development of a robust antifouling deposition layer is therefore important for practical applications.

Methyl acrylate was found to be hydrophilic and has demonstrated its antifouling property when grafted on polysulfone membrane via UV (ultraviolet-visible) irradiation [13]. Ethylene glycol derivatives were reported to be less adhesive to protein and natural organic matters [24-26]. Blending low molecular ethylene glycol derivatives into the polymer for membrane fabrication [17, 26] or grafting via UV [13] have been extensively studied, but both methods either have potential risks of leakage of modifiers with low molecular weights and reducing membrane mechanical strength, or rely on the harsh and complicated reaction conditions.

In this work, a group of synthesized hydrophilic polymers including one type of random copolymer and two types of homopolymer were deposited onto the PES membrane surface. It is expected to use these polymer-based modifiers to improve the membrane hydrophilicity via the water affinitive unit of glyceryl monomethacrylate (GLMMA), and to strengthen the interaction with PES membrane surface via the membrane affinitive unit of poly(ethylene glycol) methyl ether acrylate (PEGA). The membrane surface chemistry, surface charge, and topography were characterized using ATR-FTIR, zeta-potential, FESEM and AFM, respectively. The fouling behaviors of the modified membranes were evaluated in a cross-flow filtration system using 0.5 wt % Bovine Serum Albumin (BSA) solutions. Subsequently, a long-term

cyclic fouling test was conducted to assess their stability during filtration and chemical cleaning. The results demonstrated the feasibility of as-synthesized copolymer in reducing organic fouling for UF membrane applications.

## **2. Methodology**

### **2.1 Materials and chemicals**

Polyethersulfone resins (PES, Ultrason® E6020P, BASF) and N, N-Dimethylformamide (DMF, Merck) were used to prepare dope solutions for membrane substrates. Bovine Serum Albumin (BSA, CAS number 9048-46-8) and Sodium hydroxide (CAS number 1310-73-2) were purchased from Sigma Aldrich to represent organic foulant and using as cleaning chemical, respectively.

### **2.2 Synthesis of random copolymer GP2, homopolymer AM2, and homopolymer GL2**

The copolymer (GP2) and homo-polymer (AM2 and GL2) were synthesized by Nippon Shokubai Co., Ltd. The chemical structures of the three macromolecules are listed in Table 1. AM 2, GL2 and GP2 are synthesized from 100% PEGA, 100% GLMMA, and a mixture of GLMMA and PEGA (molar ratio 80% to 20%), respectively. In brief, Pure water (50.7 g) was charged in a flask under a nitrogen atmosphere and the solution was preheated at 80 °C in an oil bath. Then, glycerol monomethacrylate (GLMMA) (4.8 g, 30 mmol), poly(ethylene glycol) methyl ether acrylate (PEGA) (57.9 g, 150 mmol), 35 wt % sodium hydrogensulfite aqueous solution (0.9 g, 3 mmol), and pure water (20 g) were constantly fed into the reaction flask for 3 h and 2 wt % sodium peroxodisulfate aqueous solution (22.5 g, 2 mmol) was fed for 3.5 h, generating GP2. Similarly, AM2 was synthesized using PEGA, and GL2 was synthesized using GLMMA. Molecular weight was measured by gel permeation chromatography. In current condition, the amount of residual monomer in the final reaction solution, measured by gas chromatography and liquid chromatography, is zero. So, the chemical composition of the final polymer is the same as the ratio of initial monomers.

### **2.3 Fabrication of UF membranes**

The PES hollow fiber UF membranes was obtained following the dry-jet wet spinning method, which was depicted in our previous work [27]. The obtained membrane has a molecular weight cut-off (MWCO) around 60,000 Dalton.

#### **2.4 Deposition of polymer modifiers onto PES hollow fiber UF membrane surfaces**

Membrane modules were prepared according to our previous work [28]. Each module consists of 6 pieces fibers with an active membrane area of  $\sim 46 \text{ cm}^2$ . The pure water permeability (PWP) was measured before conducting the modification, and only the membrane modules with similar PWP were selected for further modification. The polymer solution (2 g/L ) was vacuumed into a hollow fiber module by a syringe and stayed in contact with the membrane for 24 hours. The modification is designed to occur on the lumen side of the hollow fibers. Then the excess solution was purged off and cleaned with DI water for several times. The modified modules were kept in DI water until further use.

#### **2.5 Membrane characterization**

All the membrane samples were freeze-dried for at least 12 hours before characterization. For surface characterizations, the hollow fiber membrane was cut open and fixed on a flat tape with the inner surface faced up properly. The surface and cross-section morphologies of the membranes, coated with a thin layer of platinum, were observed by a Field-emission scanning electron microscopy (JSM-7600F) from JEOL. The surface roughness was estimated by atomic force microscope technology (AFM, Park XE-100) in a non-contact mode.

Attenuated total reflection-Fourier transform infrared spectra (ATR-FTIR) of the membranes were characterized by an infrared spectrometer (Shimadzu Prestige-21, Japan). The water contact angle of the membrane surfaces was measured using a goniometer (Contact Angle System OCA, Data Physics Instruments GmbH, Singapore). The data reported are based on 8 replicate samples. The zeta potentials of membrane skin layer were characterized using an electro-kinetic analyzer (SurPASS<sup>TM</sup> 3, Anton Paar) with 10 mM NaCl aqueous solution acting as the background electrolyte solution [29].



## 2.6 Membrane fouling tests

BSA fouling tests were conducted at constant pressure mode in a typical cross-flow filtration setup as mentioned elsewhere [6]. In brief, a membrane module was mounted in a circulated testing loop. Deionized water was pumped to permeate through the membrane at a surface flow velocity of  $\sim 0.8 \text{ m}\cdot\text{s}^{-1}$  at a constant pressure of 1 bar. The initial pure water flux of the module, labelled as  $J_{BF}$ , was recorded. Then, the feed water was replaced with a BSA solution (0.5 wt %) for fouling tests at the same mode. Water flux during the fouling tests,  $J_F$ , of each membrane module was calculated and was recorded periodically for 120 minutes. After the 120-min fouling test, the membrane was on-line washed with DI water for 15 mins and then cleaned with a NaOH solution (0.2 wt %) for 15 min. The Flux after chemical cleaning, denoted as  $J_{AF}$ , was tested and recorded. One complete testing loop of  $J_{BF}$ ,  $J_F$ ,  $J_{AF}$  is counted as one cycle. For the cyclic fouling tests, three continuously cycles were conducted.

Flux recovery (FR) and membrane resistances were calculated as follows to appraise the fouling performance of membranes [30, 31]:

$$FR (\%) = J_{AF}/J_{BF} \times 100\% \quad (1)$$

Intrinsic membrane resistance ( $R_m$ ):

$$R_m = \frac{TMP}{\mu \times J_{BF}} \quad (2)$$

Irreversible resistance ( $R_{ir}$ ):

$$R_{ir} = \frac{TMP}{\mu \times J_{AF}} - R_m \quad (3)$$

Reversible resistance ( $R_r$ ):

$$R_r = \frac{TMP}{\mu \times J_F} - R_m - R_{ir} \quad (4)$$

Total resistance ( $R_t$ ):

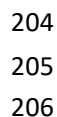
$$R_t = R_m + R_{ir} + R_r \quad (5)$$

where TMP is transmembrane pressure (100 kPa) and  $\mu$  is the viscosity of permeate.

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### 3.2 Membrane surface properties and morphologies

Three types of polymer modifiers with the same chemical segment and different molar ratio were deposited onto three PES membrane surfaces, respectively. These membrane surfaces were characterized via ATR-FTIR as illustrated in Figure 2. The peak at  $1298\text{ cm}^{-1}$  corresponds to S=O from PES UF membrane. Compared to the pristine membrane, a new peak can be observed for all three modified membrane surfaces at  $1732\text{ cm}^{-1}$  assigned to C=O group from GLMMA and PEGA segments in polymer modifiers, which verifies the existence of the modifiers on the PES surface.

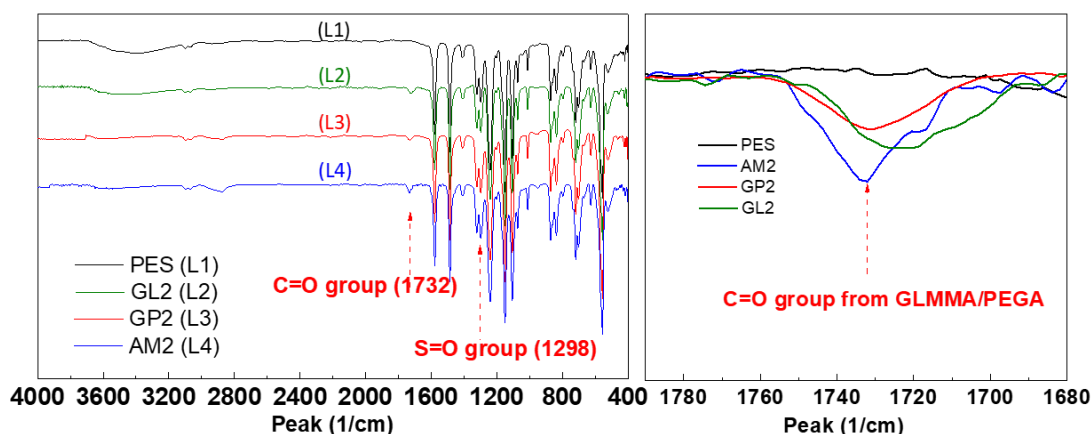


Figure 2. ATR-FTIR spectra of the control membrane and copolymers/homo-polymer modified membrane. (a) Full spectra FTIR results; (b) enlarged spectra of the target specific peaks. Lines (1)-(4) stand for the PES, GL2, GP2, AM2 adsorbed PES membranes, respectively.

The surface charge was characterized by Zeta potential as shown in Figure 3. All the membranes show a similar charge profile in the pH values ranging from 2 to 10. It is noted that GL2 (100% GLMMA unit) has a higher zeta potential value than AM2 (100% PEGA unit) in the pH range of 4 to 10. It reveals that the segment unit GLMMA is more positively charged than the PEGA unit in the basic pH range which may due to R-OH group in GLMMA unit can accept a proton ( $\text{H}^+$ ) to form  $\text{R-OH}_2^+$ .

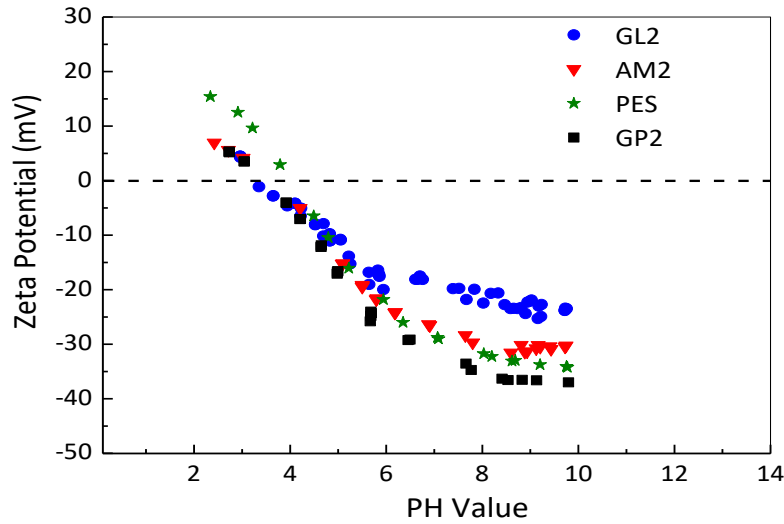


Figure 3. Zeta Potential as a function of pH of control PES membrane and modified membranes.

Figure 4 presents the surface images of PES membrane, GL2, GP2, AM2 modified PES membranes, respectively. The surface of the membranes coated with polymer modifiers is less porous than that of control PES membrane due to the deposition of the modifiers on the surface and the covering of the large pores. The inserted images show the water contact angles of the modified membranes and control membrane. The data of the water contact angles follow the trend as  $GL2 < GP2 < AM2/PES$ , which is attributed to the portion of hydrophilic GLMMA unit. The GL2 with 100% GLMMA unit has the lowest contact angle, and the GP2 has a moderate low contact angle with 20% GLMMA unit. It is expected that these deposited hydrophilic polymers are stable enough and can reduce the membrane contamination with organic foulants.

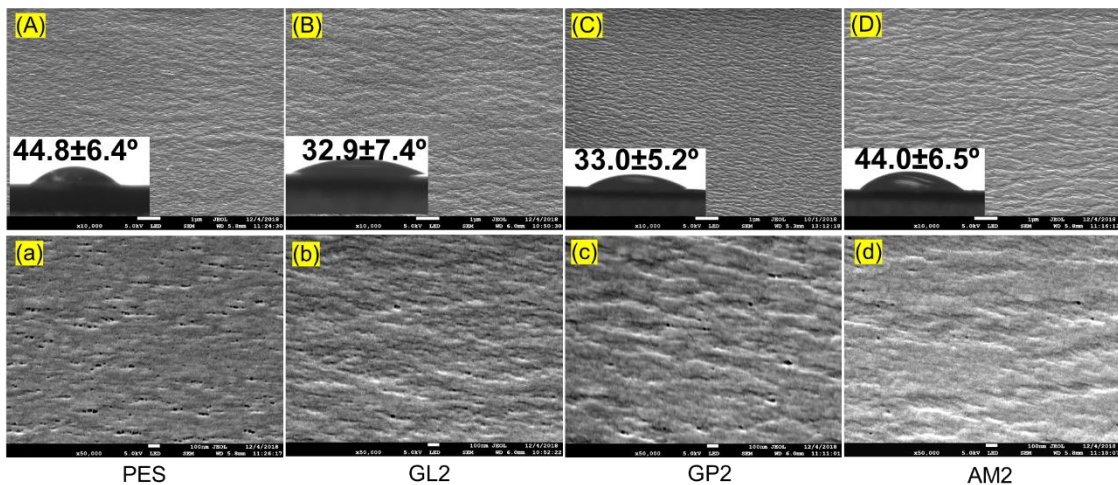


Figure 4. FESEM images of membrane surface (A) PES, (B) GL2, (C) GP2, and (D) AM2. The scale bar in the first row stands for 1  $\mu$ m and 100 nm in the second row.

AFM was utilized to characterize the surface roughness after surface modification. It is observed from Table 2 that the root mean square roughness ( $R_q$ ), mean roughness ( $R_a$ ) and maximum peak-to-valley distance ( $R_z$ ) of the GP2 are lower than those of the control PES, AM2, and GL2, indicating the more smooth surface of the GP2 membrane. It is expected that GP2 and GL2 membrane could benefit from this reduced roughness when foulants exist in feed solution during filtration.

Table 2. Roughness of the control membrane and polymer-coated membranes.

Polymer modifier	$R_q$ (nm)	$R_a$ (nm)	$R_z$ (nm)
PES	$7.2 \pm 2.2$	$5.9 \pm 1.9$	$49.4 \pm 12.8$
GL2	$4.5 \pm 0.6$	$3.6 \pm 0.5$	$35.9 \pm 5.3$
GP2	$3.7 \pm 0.3$	$2.8 \pm 0.3$	$46.0 \pm 1.9$
AM2	$7.2 \pm 0.2$	$5.8 \pm 0.1$	$58.8 \pm 13.4$

### 3.3. UF membrane intrinsic permeability and fouling study

The pure water permeability (PWP) of membranes is presented in Table 3. The absolute initial PWP of the GL2, GP2 and AM2 decreases ~60% after the modification from 253 LMH/bar to ~100 LMH/bar, due to the mass transfer resistance induced by the additional polymer layer. The additional layer may cover some visible large surface pores according to the FESEM images in Figure 4, resulting in the decrease in PWP. The decrement in MWCO in Table 3 further verifies that the pore size was narrowed when the polymer adsorbed onto PES UF membranes.

Table 3. Intrinsic permeability of the control membrane and the modified membranes.

Membrane code	$PWP$ (LMH/bar)	$MWCO$ (Normalized, %) <sup>(1)</sup>	$BSA$ fouling flux (LMH) <sup>(2)</sup>
PES	$253 \pm 48$	100	$58 \pm 3$
GL2	$101 \pm 21$	98	$59 \pm 15$
GP2	$104 \pm 10$	79	$73 \pm 7$

AM2

103±11

70

66±3

Note: (1) The MWCO of the modified membranes were tested and normalized with the MWCO of control PES membrane; (2) BSA fouling flux means the water flux using 0.5 wt % BSA solution under the pressure of 1 bar, the reported flux is the average data of the last 30 minutes in the 2-hour BSA fouling test.

On the other hand, the modified membranes perform better in terms of normalized permeability, absolute permeability, and flux recovery rate during the BSA fouling tests according to Figure 5 and Figure 6. The values of normalized permeability, absolute permeability, and recovery rate are in the order of GP2> AM2> GL2>PES. As indicated in Figure 5 (Left), PES UF membrane deposited with GP2, GL2 and AM2 maintain 50% to 85% of their initial permeability during BSA fouling tests, while PES control membrane loss ~70% of its initial permeability. Flux recovery rate is an excellent index to evaluate membrane antifouling performance. The modified membranes show a higher flux recovery rate as compared with control PES membrane. The typical flux recovery rate is 95%, 85%, 60% for GP2, AM2 and control PES, respectively.

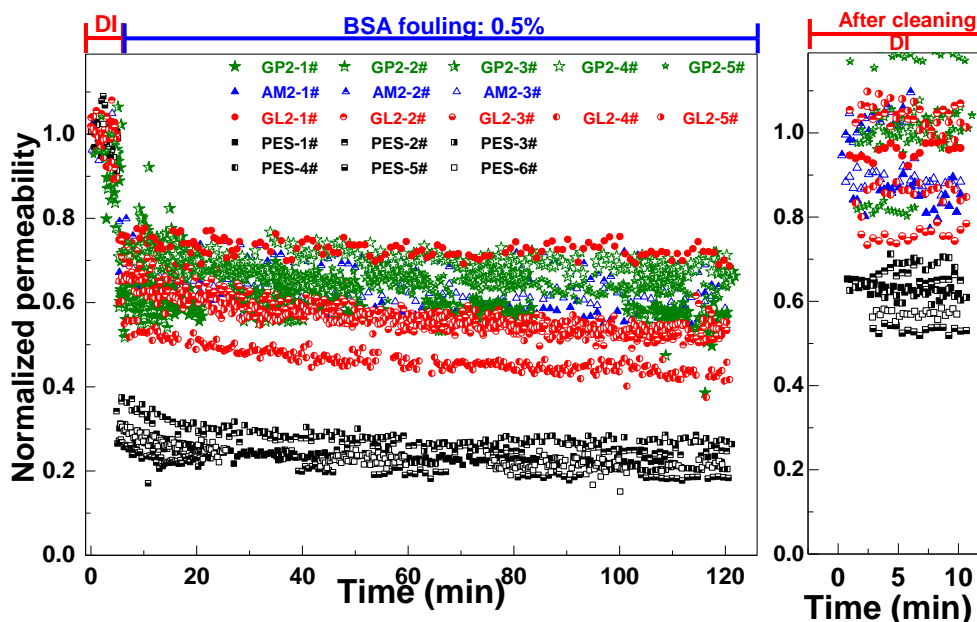
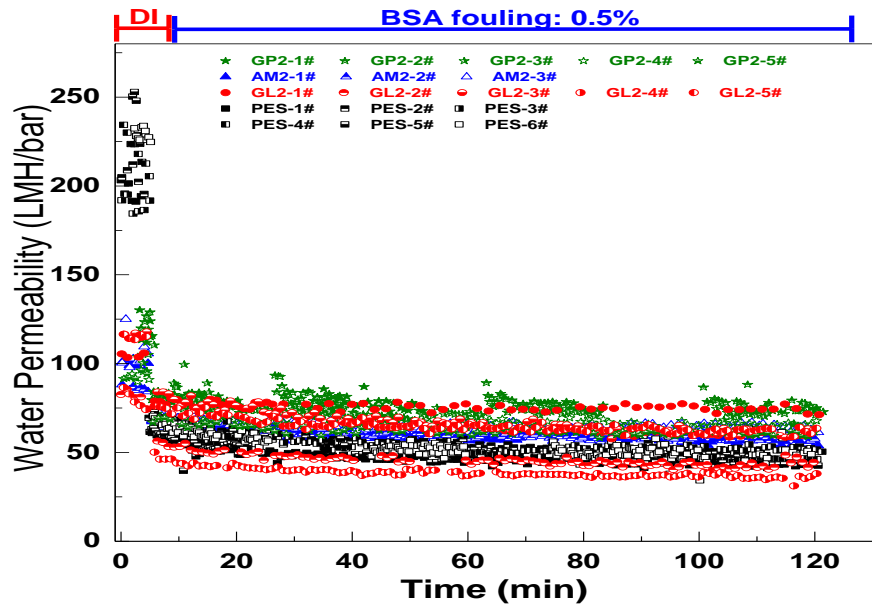
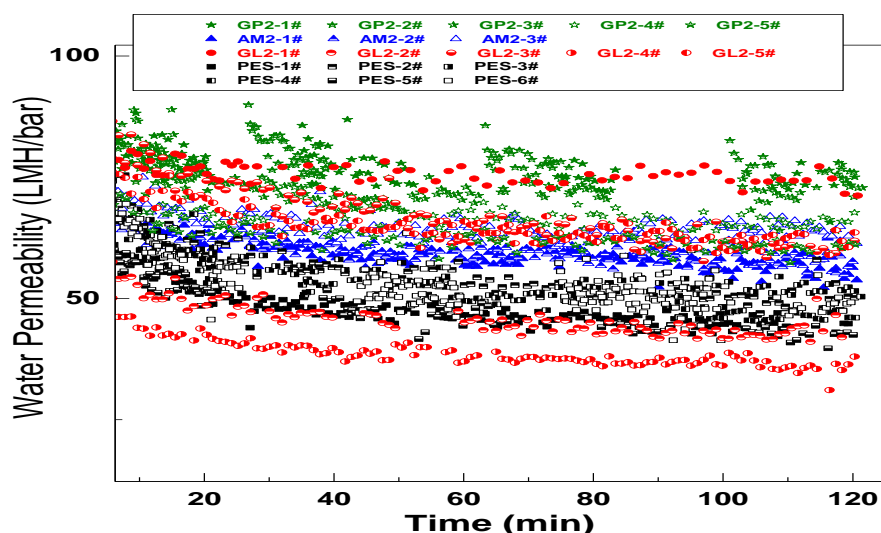


Figure 5. Normalized water permeability of as-prepared membranes under high concentration foulant. Testing conditions: constant pressure at 1 bar; Time 0-5min, DI water as feed; Time 6-120min, 0.5% BSA solution as feed. The numbers in the legends mean the replicate fouling tests of each membrane type.

It is noted in Table 3 that the initial pure water permeability of the modified membrane is obviously lower than that of the control PES membrane. The absolute permeability during BSA fouling test, a good indicator of membrane energy consumption, is also studied in this work and the results are shown in Figure 6. Generally, membrane fouling took place immediately when the membrane contacts with foulants, indicated by the sudden water permeability decline. Subsequently, a continuous gradual reduction of water flux was observed for the rest of the testing period. Although the modified membranes show a lower initial permeability, they outperform the control membrane in treating water containing foulants. The values of the water permeability follow the sequence of GP2>AM2>PES. The results suggest that the PES UF membrane modified with a hydrophilic thin layer of copolymers (GP2) is a practical and straightforward way to reduce membrane fouling with the benefits of simple modification procedures, high water permeability and good flux recovery rate. In addition, these copolymer layers are highly stable after cleaning with a 0.2 wt % NaOH aqueous solution for three times in the cyclic fouling test, indicated by the unchanged water permeability.



(a)



(b)

Figure 6. (a) full profile view and (b) enlarged view of the permeability dependence on testing time of control membrane and polymer modified membranes. The numbers in the legends mean the replicate fouling tests of each membrane type.

The membrane resistance profiles are summarized in Table 4. It reveals that the modified membranes have a higher intrinsic membrane resistance than the control PES membrane due to the additional polymer layer. The irreversible resistance, reversible resistance and total resistance of modified membranes, especially GP2 membrane, are lower than those of control PES membrane during fouling testing.

Table 4. Membrane resistance profiles

Membrane code	$R_m (\times 10^{11} \text{ m}^{-1})$	$R_{ir} (\times 10^{11} \text{ m}^{-1})$	$R_r (\times 10^{11} \text{ m}^{-1})$	$R_t (\times 10^{11} \text{ m}^{-1})$
GL2	$42.3 \pm 8.0$	$3.6 \pm 4.7$	$32.5 \pm 19.8$	$78.5 \pm 24.4$
GP2	$37.7 \pm 4.4$	$0.7 \pm 1.6$	$19.9 \pm 2.5$	$58.4 \pm 5.0$
AM2	$42.0 \pm 4.3$	$5.1 \pm 3.2$	$22.3 \pm 2.9$	$69.4 \pm 5.5$
PES	$19.0 \pm 2.6$	$11.7 \pm 2.4$	$49.8 \pm 4.9$	$80.4 \pm 5.8$

Note:  $R_m$ ,  $R_{ir}$ ,  $R_r$ , and  $R_t$  represents the intrinsic membrane resistance, irreversible resistance,



reversible resistance, and total resistance, respectively.

### **3.4 Evaluation of the stability of the deposition layer**

#### **3.4.1 Cyclic fouling tests**

Cyclic fouling tests were conducted to evaluate the deposition layer's stability during the chemical cleaning, which is a necessary step in practical applications. Figure 7 shows the cyclic fouling test results of modified membranes. In general, the modified membrane's pure water permeability was supposed to increase to a comparable value as of PES membrane if the deposition layer is removed from the membrane surface. The unchanged PWP and recovery rate of all the modified membranes at the initial stage of all three cycles indicates that the deposition layers are firmly attached on the membrane surface throughout the cyclic fouling test and chemical cleaning. The dotted green and black lines were depicted to project the trend of pure water permeability of the GP2 and PES membranes in long-term service. Although the GP2 membrane shows a significant lower pure water permeability than that of PES control membrane, the GP2 membrane excels PES membrane in BSA filtration process. The pure water permeability of the GP2 membrane is almost maintained around 95 LMH/bar, while PES membrane dropped from 200 LMH/bar to 85 LMH/bar, which is below that of the GP2 membrane after three cycles of fouling test. To summarize, the GP2 exhibits better performance than the other three membranes in view of the stability, fouling filtration permeability, and flux recovery rate.

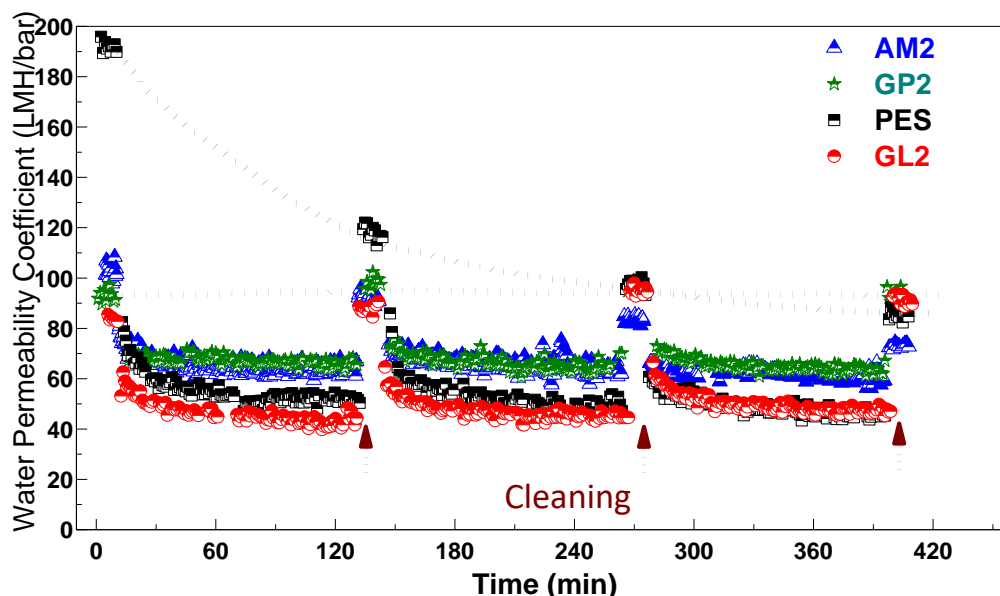


Figure 7. Long-term cyclic fouling test of a representative sample of each type of membrane. The membranes were cleaned with DI water and 0.2 wt % NaOH solution during each fouling cycle. The dotted angles point out the time of cleaning, and dotted lines were drawn to illustrating the trend of pure water permeability of the control membrane and GP2 modified membrane.

### 3.4.2 Membrane surface chemistry after cyclic fouling test

Figure 8 shows the ATR-FTIR spectra of the pristine membranes (L1-L4) and chemical cleaned membranes after three cyclic fouling testing (L5-L8). Compared to the corresponding pristine membranes, an additional peak is shown in the fouled membranes at  $1656\text{ cm}^{-1}$  which is the characteristic peak of BSA protein due to the C=O stretching mode of amide I [32]. The existence of BSA peak even after chemical cleaning indicates that the membrane even modified with polymer can not permanently avoid fouling, but the decreased peak area project that these modifier can reduce the degree of fouling. The peak at  $1732\text{ cm}^{-1}$ , characteristic peak of C=O group in modifier, evidenced by ATR-FTIR even covered with BSA foulant layer after chemical cleaning in the cyclic fouling testing confirms the existence of the assembled modified layer.

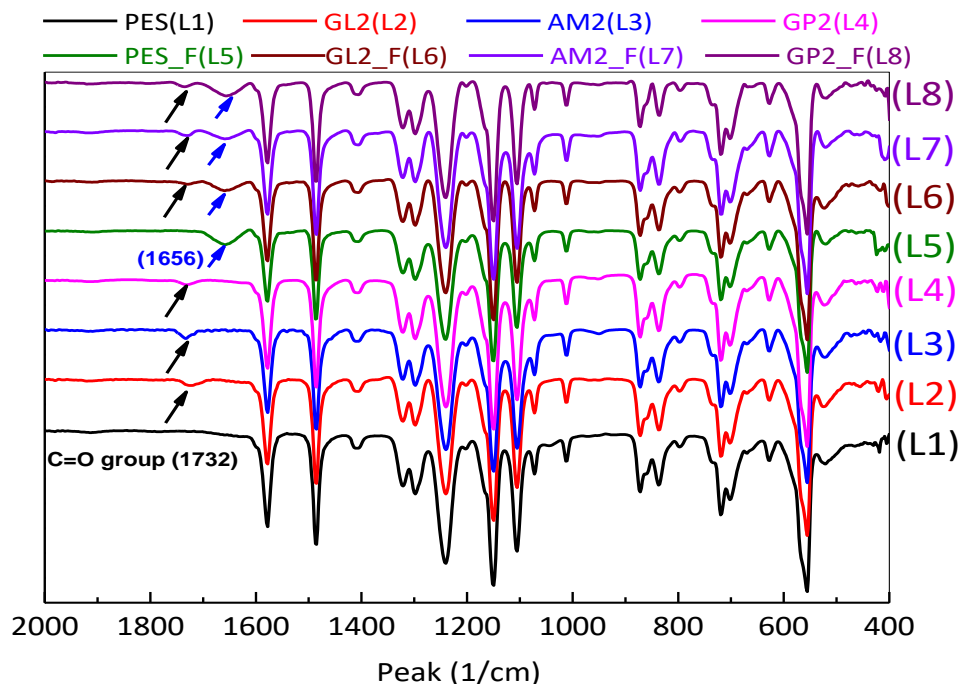


Figure 8. FTIR spectra of clean membranes (L1-L4) and chemical cleaned membrane after BSA fouling test (L5-L8). Here, the sample label ended with \_F means the chemical cleaned membrane after fouling test.

#### 4. Conclusions

Three types of synthesized polymer modifiers were utilized to enhance anti-fouling property of PES UF membrane via direct coating and their response to BSA foulant were evaluated. The membranes' stability in fouling and chemical cleaning were evaluated as well in the current study. Several findings can be concluded as follows:

- (1) The chemical composition, hydrophilicity and molecular weight of the synthesized polymer were characterized. These macromolecules are hydrophilic and have a molecule weight of 43000, 47000 and 54000 for AM2, GL2 and GP2, respectively.
- (2) The morphology, water permeability, pore size and chemistry of the control PES and polymer-modified PES UF membranes were systemically investigated. It was found that these polymers can deposit on the lumen side of hollow fiber membrane and reduce the membrane's pure water permeability and pore size.
- (3) The modified membranes show an average 26% increment of water permeability during BSA fouling testing as well as higher flux recovery rate compared with the control PES membrane although the modified membranes exhibit a lower initial pure water permeability.

The random copolymer synthesised from two monomers shows a good chemical stability and antifouling effect during the fouling test.

(4) The cyclic fouling testing and FTIR characterization demonstrated the stability of the deposited polymer layers in long-term testing and chemical cleaning. The promising result suggests the feasibility of using this group of hydrophilic polymers in developing antifouling UF membranes.

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